ON THE MAGNETIC SUSCEPTIBILITY OF PURE AND IMPURE COPPER METAL

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ABSTRACT. Temperature variation of magnetic susceptibility of copper metal and copper metal with trace of nickel impurity have been measured. An accurate susceptibility balance with an electronic detection system has been described. The mass susceptibility of pure copper is independent of temperature and copper contaminated with nickel shows anomalous temperature variation. A theoretical estimate of the susceptibility of copper has been made.

INTRODUCTION

The magnetic susceptibility of high purity copper has been the subject of investigation in a number of papers. de Haas and van Alphen (1933) observed a monotonic increase of susceptibility with decreasing temperature. Bitter *et al* (1941) found that the susceptibility first increased by 3% as the temperature was lowered from 300°K to 63°K, but subsequently decreased by about 35% between 63°K and 14°K. Bowers (1956) reexamined the magnetic susceptibility of high purity copper between 300°K and 1.5°*K* and reported a temperature independent susceptibility. Bower's result confirms the predictions of the free electron model, wherein one would expect the magnetic susceptibility of copper metal to be substantially independent of temperature. Recently van Itterbeek and Du Chateau (1957) have observed that the susceptibility of copper metal decreased by 18% between 17°K and 1.62°K. This decrease has been ascribed to the presence of trace impurities of Ni and Fe. Kaufmann and Starr's (1943) earlier measurement on moderately pure copper metal and dilute Cu-Ni alloys also indicated an anomalous temperature variation of susceptibility both for the pure metal and the alloy. We suspect that the anomalous variation of magnetic susceptibility reported by different workers, is due to the contamination of copper with magnetic impurities. With this in view the measurement of magnetic susceptibility of very pure copper and copper with trace nickel impurity has been undertaken.

EXPERIMENTAL

The measurements undertaken in this work require very accurate determination of mass susceptibilities of the order of 10^{-7} C.G.S. units; hence a magnetic balance with a cryostat suitable for the purpose was designed and built in this laboratory following the basic design of quartz fibre microbalance of Bose (1947).

The apparatus of Bose was very convenient for accurate single crystal work. But the whole arrangement was very delicate and difficult to handle and because of the manual control it was not free from personal errors and often external disturbing factors and zero shifts made it difficult to have reproducible value. Therefore several modifications were incorporated to increase the sensitivity, stability and robustness of the balance.

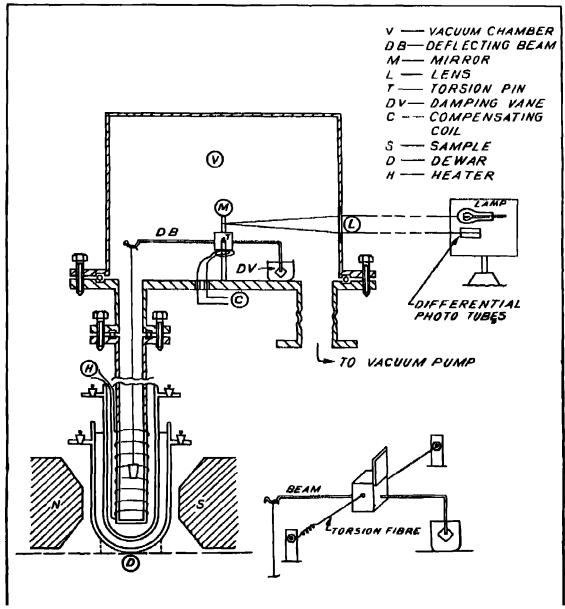

FIG. 1 MAGNETIC MICRO BALANCE

The balance beam was made from quartz rod and (fig. 1) suspended at the middle with horizontally stretched phosphor bronze strips (30 mm × 0.287 mm × 0.022 mm) cemented to the beam. The other ends of these strips weres oldered to the ends of two torsion pins passing horizontally through two upright rectangular brass pieces. The specimen to be studied was suspended to one end of the balance beam with a fine tungsten fibre. In order to protect the balance from spurious vibrations a mica damping vane, dipping in silicone oil, was attached to the other end of the balance beam. The whole assembly was enclosed in a brass case provided with a glass window. Provisions were made to create a vacuum of the order of 10^{-5} mm of Hg in the experimental chamber. This was necessary to avoid convection disturbance and also for excluding the contamination of the sample due to

oxidation. A photoelectric difference amplifier was employed for observing the magnetic force. A spot of light from a stabilised 12 volt lamp was focussed by a lens system and after reflection from the mirror attached to the balance beam was again focussed by another lens system and was allowed to illuminate the cathodes of two photoelectric tubes mounted horizontally one over another. The output from the phototubes was fed to a difference amplifier as shown in Fig 2. The

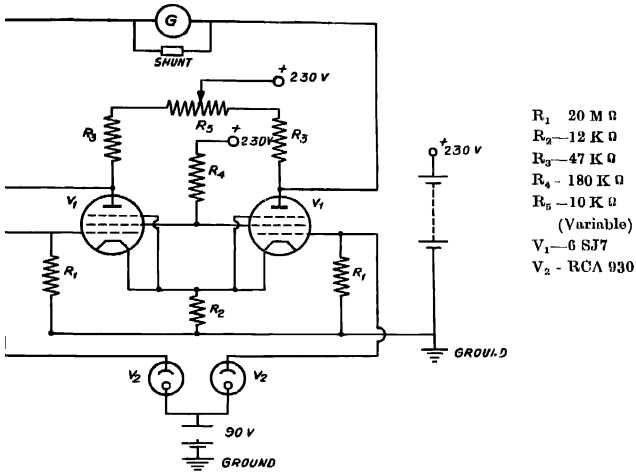

Fig. 2. Schematic diagram of the detecting Circuit

difference current was amplified and fed to a shunted galvanometer, and the deflection in the output galvanometer was always made full scale (100 divisions) by adjusting the shunt to the proper value. This was done to maintain a constant deflection sensitivity. The zero drift in the amplifier was appreciable for the first ten minutes, but no further zero drift was observed even when the amplifier was used for 4 to 5 hours.

The restoration of the balance beam to the original position was effected with a compensating coil of 1 cm diameter and 250 turns of insulated copper wire (47 SWG) fixed horizontally to the beam of the balance with its axis passing through the centre of the beam. This follows the method of Neogy and Lal (1962). The current through the coil was regulated by means of five variable resistances in series with the coil. The coil being placed in the stray field H of the magnet experienced a couple (NHIA/10)g.-cm where N, the number of turns of the coil and A, the area of cross section of the coil and I, the current through the coil in amperes. If I was the current required to compensate the torque on the sample

of mass m and mass susceptibility χ and I_s for the standard sample of mass m_s, mass suceptibility χ_s, (Bose *et al.*, 1963) then χ is given by ;

$$\chi = \frac{I}{I_s}\frac{m_s}{m}\left[\chi_s - \frac{k_a}{\rho_s}\right] + \frac{k_a}{\rho}$$

where K_a the volume susceptibility of air at a temperature T°K; ρ_s and ρ the densities of standard sample and the sample under study, respectively. The current in each case was estimated by measuring the potential drop, across a standard resistance of 10 ohms with a microvolt Kaycee potentiometer. Each measurement was repeated five times and error was found to be less than 0.1%. An air cooled electromagnet of field 10000 gauss with a gap of 5 cm was used.

The temperature of the sample was varied from 1000°K to 90°K. Liquid oxygen cryostat was constructed following the design of Bose *et al.* (1963). In this arrangement any temperature between 300°K to 90°K was kept constant for a long time within 0.5°K. The control was made automatic with the help of a gas-thermometer relay system, which operated a non-inductive electric heater in the experimental chamber. The temperature was read with a calibrated copper constantan thermocouple.

The calibration of the balance was done with conductivity water whose mass susceptibility was taken to be -7.214×10^{-7} emu/gm at 300°K. Mass susceptibility of five crystals of potassium chloride supplied by Harshaw and Co., U.S A., was compared with the conductivity water and the mean value was found to be -5.179×10^{-7} emu/gm at 300°K which was in agreement with the previously reported values to within 0.2%. This crystal was used as a secondary standard in subsequent measurements. For a further check five crystals of sodium chloride were grown in this laboratory and the mass susceptibility was compared with the KCl crystal. The observed mean value was found to be -4.995×10^{-7} emu/gm at 300°K which agreed with the earlier values (Chowdhury, 1959) to within 0.5%

RESULTS AND DISCUSSION

The pure copper specimen (A) was supplied by Johnson and Mathey and had the following impurity contents :

Element	Approx. estimate of quantity present
Silver	0.0002%
Lead	0.0004%
Nickel	0.0003%

The mass susceptibility was found to be -0.91×10^{-7} emu/gm which is higher than the value observed by van Itterbeek and W. Du Chateau (1957) by about 6%. The specimen showed no field dependence even at lower fields. In table I we

have collected the theoretical values which may be compared with our experimental value. χ_s is the free electron value for the spin contribution (Korring, 1950). The value of core susceptibility χ_c is derived from direct calculations from the electronic wave functions. The orbital contribution χ_0 used is the Landau-Peierls free electron value. χ_N is the nuclear susceptibility which is about 1/5th of the value of χ_S (Bowers, 1956). It can be seen that there is no serious disparity between calculated and the experimental value (χ_{Th} the χ_{Ex}) The value obtained by van Itterbeek and the present result are in good agreement amongst themselves and closer to the theoretically estimated value

TABLE I

Theoretical estimate of the mass susceptibility of copper in c.mu/gm, compared to the experimental

	χ_{Th}	χ_{Ex}
χ_C	$-1\ 91\times10^{-7}$	$-0\ 83\times10^{-7}$ (Bowers)
χ_S	$+1\ 10\times10^{-5}$	$-0\ 87\times10^{-7}$ (Van Itterbeek)
χ_N	$+0\ 22\times10^{-7}$	-0.80×10^{-7} (Kaufmann & Starr)
χ_O	-0.37×10^{-7}	
Total χ_{Th}	-0.96×10^{-7}	-0.91×10^{-7} (Present Work)

The temperature dependence of the susceptibility observed by us does not agree with that found by earlier workers. Fig. 3 shows that sample A has temperature independent susceptibility between 600°K to 100°K. This is in good agreement with Bowers' result on copper metal (99.999% purity). A small temperature dependent term observed by Bowers has been ascribed by him to the presence of residual paramagnetic impurity as well as nuclear susceptibility. In the temperature range we have worked the nuclear susceptibility should contribute a temperature dependent term ~0.3% which is just outside our experimental accuracy. Thus it seems likely that the susceptibility of pure copper is substantially independent of temperature.

The mass susceptibility of specimen B (deliberately contaminated specimen A with nickel)w as found to be $-0\ 92\times10^{-7}$ emu/gm at 295°K. This specimen showed temperature independent susceptibility in the high temperature range (295°K to 600°K) but in the low temperature range (295°K to 100°K) it showed an increase of diamagnetic susceptibility by about 7.5%. This temperature variation is similar to that observed by Bitter *et al.* (1941) on moderately pure copper specimen.

The specimen C was prepared in an induction furnace by melting appropriate quantity of copper and nickel in recrystallized alumina crucible using helium

atmosphere. The details of the method of preparation have already been described by Dutta Roy (1961). The alloy contained 99.9 weight percent of copper and 0.1 weight percent of nickel. The sample was annealed for 24 hours in a vacuum annealing furnace at 500°C. The mass susceptibility of this specimen was found out to be -0.758×10^{-7} emu/gm at 295°K and was field independent at lower fields The diamagnetic susceptibility decreased monotonically with the lowering of temperature (600°K to 100°K). This variation (fig. 3) is somewhat

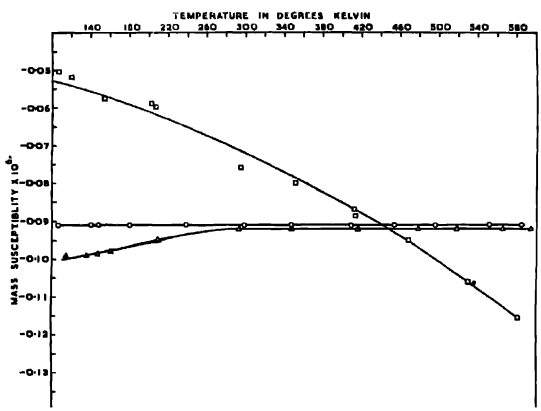

FIG 3 SUSCEPTIBILITY VARIATION OF PURE AND IMPURE COPPER
O—PURE COPPER (A)
▲—IMPURE COPPER (B)
□—IMPURE COPPER (C)

expected because nickel, if present as trace impurity in copper, contributes a paramagnetic term due to the presence of 3*d* holes in the alloy. But Curie-Weiss law does not account for this observed temperature variation and only a three constant formula of the type $AT+B+C/T$ suggested by Kaufmann and Starr (1943) for copper-nickel alloys gives an approximate fit to the experimental temperature susceptibility curve (fig. 3). We have not attempted a rigorous analysis of the experimental results on the basis of the above three constant formula since the origin of the AT term is obscure and no theory of magnetism suggests such a term. Also the observed temperature variation in specimen B and C can not be connected to the thermal expansion (or contraction), otherwise similar temperature variation of mass susceptibility would have been observed in the case of pure copper (specimen A).

In conclusion the present experimental result on pure copper suggests that the susceptibility is substantially independent of temperature but in impure copper

with nickel as trace impurity susceptibility shows an anomalous temperature variation.

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